

## Radiation Stability of Metal Nanowires

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**Abstract.** The aim of this work is to investigate the radiation stability of pure nickel and iron–nickel  $\text{Fe}_{0.56}\text{Ni}_{0.44}$  alloy nanowires fabricated by matrix synthesis using polymer track membranes and  $\text{Ar}^+$  and  $\text{Xe}^+$  ( $E = 20 \text{ keV}$ ,  $j = 300 \mu\text{A}/\text{cm}^2$ ) beam irradiation. The dependence of the stability of nanowires on their diameter, fluence, and type of implanted ions is investigated. The assumption that the thermalized regions of dense cascades of atomic displacements (thermal spikes) play an important role in the nanowire structure change is made. These regions are nanosized zones of explosive energy release and heated to several thousands of degrees.

### 1. Introduction

In recent years, scientists have been increasingly interested in the production, investigation, and application of nanosized materials. Among these materials is a promising type, namely arrays of one-dimensional metal structures, in other words, nanowires (NWs). Arrays of NWs made of copper and silver are interesting as ion and electron emitters (cold cathodes), whereas NWs made of iron are promising as magnetic materials (sensors, materials for high-density magnetic recording).

Among the important characteristics of the NW arrays is their stability. It is known [1] that the specific geometry and the developed surface lead to their lower (compared with volume analogues) chemical and thermal stability. According to preliminary results, the radiation stability of these arrays is different from that of volume materials. The study of the radiation stability is of interest because of at least two factors.

First, radiation treatment is a kind of modification and control of the properties of such NWs.

Second, radiation resistance, the ability to retain properties under different radiation conditions, in many cases is one of the most important service parameters.

It should also be noted that, in addition to the practical aspect, the issue of structural changes under irradiation is of independent theoretical interest. In contrast to the studies of radiation defects in volume metals, there is a small number of works dedicated to nanostructures of this kind. The main part of these studies is devoted to materials with nanosized grains. For example, it is noticed in [1] that



among features of nanostructures can be the inability to accumulate radiation defects due to the fact that such defects can immediately break the surface.

Among several works actually dedicated to the study of NWs, articles on the modeling of the impact of ion beams on metal NWs using molecular dynamics methods [2, 3, 4] should be noted.

In addition to the works modeling of radiation effects, there are works devoted to the study of the radiation impact on the metal NWs. For example, a method for the ion beam modification of Ni and Co NWs 200 nm in diameter is described in [5]. These NWs fabricated by template synthesis using a porous alumina oxide were irradiated with 3-MeV  $\text{Cl}^{2+}$  ions at a fluence of  $10^{15} \text{ cm}^{-2}$ . As a result, an oxidation layer on the surface of the NWs was reduced, which was supported by high-resolution TEM. The features of the surface structure changes were investigated under such irradiation.

In [6], silver NWs 120 nm in diameter and 20  $\mu\text{m}$  in length were irradiated at room temperature with 5-MeV  $\text{He}^+$  ions at a beam current of 50 nA. Insignificant changes at a fluence of  $5 \cdot 10^{15} \text{ cm}^{-2}$  were observed, whereas the initially crystal structure of NWs was transformed into the amorphous structure at a fluence of more than  $8 \cdot 10^{16} \text{ cm}^{-2}$ .

In [7], silver NWs were irradiated with 3-MeV protons (beam current of 50 nA) at room temperature. Under irradiation with fluence of  $10^{14}$ - $10^{15} \text{ cm}^{-2}$ , NWs were welded in contact areas to form a kind of grid of nanowires.

In [8], 5-MeV carbon ion irradiation-induced changes in the electrical conductivity of silver NWs were studied at different ion fluences ranging from  $10^{12}$  to  $10^{16} \text{ cm}^{-2}$ . The electrical conductivity increases and, then, decreases with increase in fluence. The first behavior was explained by the formation of contacts between the wires; the second, by an increased defectiveness in some wires.

In our work we investigated some points of radiation stability of NWs made of 3d-metals, namely pure nickel and iron-nickel  $\text{Fe}_{0.56}\text{Ni}_{0.44}$  alloy. The effects of the fluence and the temperature of a target on the stability of NW arrays were investigated upon irradiation with  $\text{Ar}^+$  and  $\text{Xe}^+$  ions ( $E = 20 \text{ keV}$ ). The used energy relates to the energy range of the most commonly used to modify the structure and properties of materials.

## 2. Experiment

The investigated NWs were fabricated by the template synthesis. Commercial track membranes with a pore diameter from 0.03 to 0.1  $\mu\text{m}$  (Joint Institute for Nuclear Research, Dubna) were used as template matrices. This deposition process is described in detail in [9, 10].

A Watts electrolyte that contains 300 g/l of  $\text{NiSO}_4 \cdot 7 \text{ H}_2\text{O}$ , 45 g/l of  $\text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}$ , and 38 g/l of  $\text{H}_3\text{BO}_2$  was used to prepare nickel NWs, at an electrolyte temperature of 50–60°C.

The  $\text{Fe}_{0.56}\text{Ni}_{0.44}$  alloy was deposited from the electrolyte of the following composition: 16 g/l of  $\text{NiSO}_4 \cdot 7 \text{ H}_2\text{O}$ , 40 g/l of  $\text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}$ ; 16 g/l of  $\text{FeSO}_4 \cdot 7 \text{ H}_2\text{O}$ ; 1-2 g/l of antiscorbutin ( $\text{C}_6\text{H}_8\text{O}_6$ ); and less than 1 g/l of sodium laurel sulfate ( $\text{NaC}_{12}\text{H}_{25}\text{SO}_4$ ).

NW arrays separated from the polymer template were irradiated with continuous  $\text{Ar}^+$  ion beams using an ILM-1 implanter equipped with a PULSAR-1M technological ion source based on a low-pressure glow discharge with a hollow cold cathode, which can operate in the continuous and pulsed-periodic modes ( $S_{\text{beam}} \sim 100 \text{ cm}^2$ ; the energy and ion current density in the continuous mode were varied in the following ranges:  $E = 5$ -50 keV,  $j = 10$ -500  $\mu\text{A}/\text{cm}^2$ ) [11].

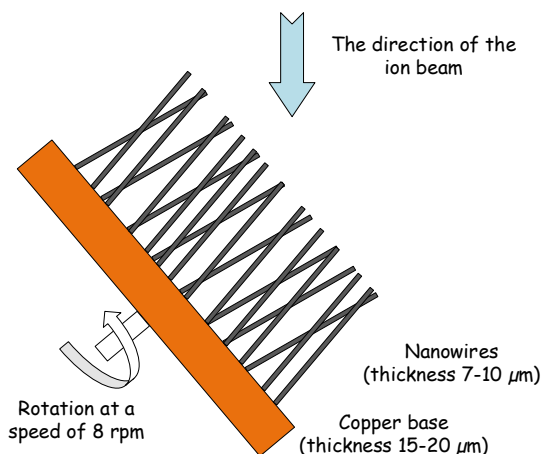
NWs were irradiated with  $\text{Ar}^+$  and  $\text{Xe}^+$  (Figure 1) onto a copper substrate with a rotated holder (angle between the ion beam axis and a normal to the substrate surface was 45°;  $E = 20 \text{ keV}$ ,  $j = 300 \mu\text{A}/\text{cm}^2$ , a rotation rate of 8 rpm) at various fluences and in several temperature conditions:

(i) irradiation with  $\text{Ar}^+$  ions,  $F = 10^{16}$ - $10^{18} \text{ cm}^{-2}$ , beam heating below 150°C (fluence were achieved in several stages to avoid sample overheating);

(ii) irradiation with  $\text{Ar}^+$  ions,  $F = 10^{16}$ - $10^{18} \text{ cm}^{-2}$ , beam heating to 550°C (fluence was continuously accumulated);

(iii) irradiation with  $\text{Xe}^+$  ions,  $F = 10^{16}$ - $10^{17} \text{ cm}^{-2}$ , beam heating to 550°C (fluence was continuously accumulated).

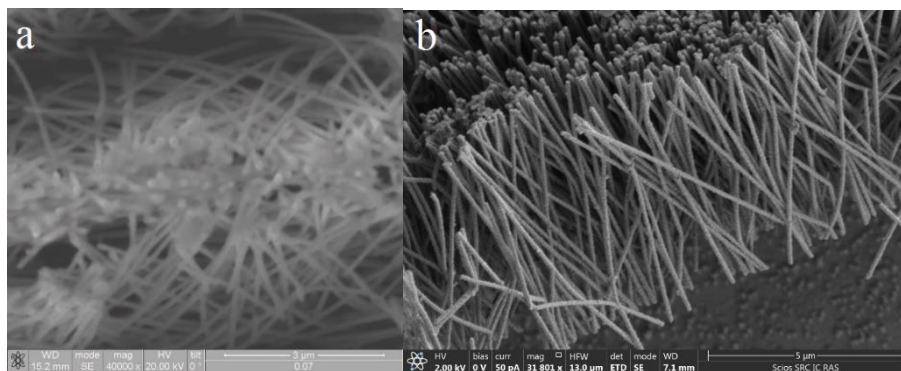
Initial and irradiated samples were investigated using an FEI Scios scanning electron microscope.



**Figure 1.** Scheme of the ion irradiation of NW assemblies.

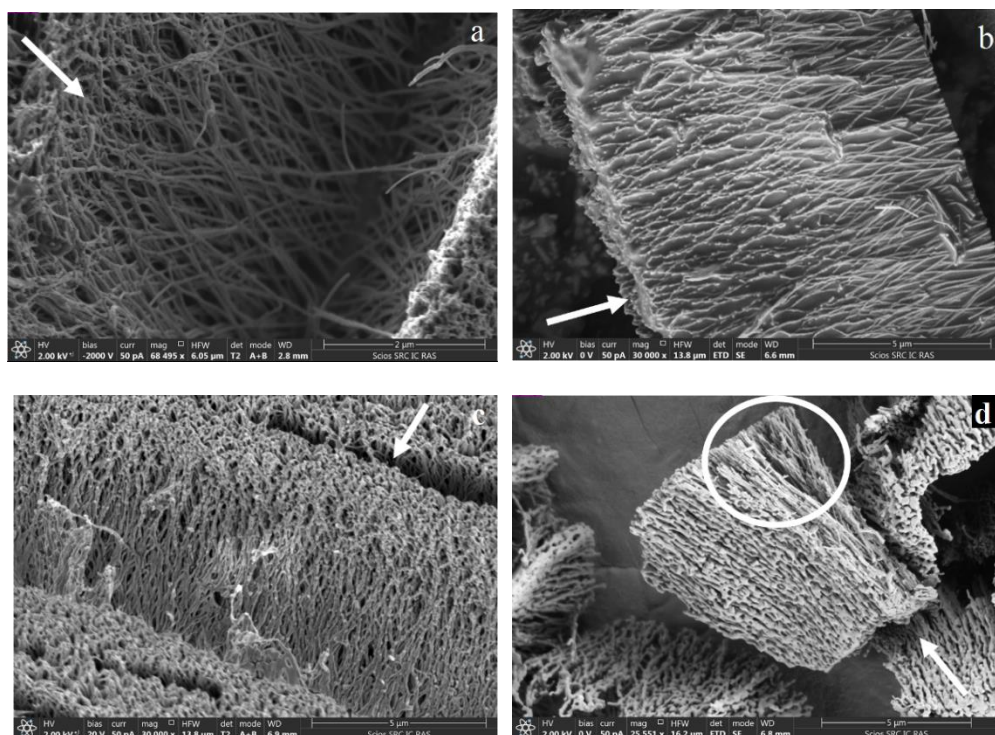
### 3. Results and discussions

Figure 2 shows scanning electron microscopy images of initial (before irradiation) NWs made of Ni with a diameter of 60 nm (Figure 2 a) and NWs made of  $\text{Fe}_{0.56}\text{Ni}_{0.44}$  alloy with a diameter of 100 nm (Figure 2 b).



**Figure 2.** Scanning electron microscopy images of (a) initial Ni NWs 60 nm in diameter and (b) FeNi NWs 100 nm in diameter.

Below, Figure 3 a demonstrates Ni NWs 60 nm in diameter after  $\text{Ar}^+$  ion irradiation. The arrow indicates the irradiation direction. At a fluence of  $10^{17} \text{ cm}^{-2}$  and an irradiation time of 1 min (Figure 3 a), melted NW tops (see the left top angle in the image) are observed. No noticeable changes are observed at a lower fluence of  $10^{16} \text{ cm}^{-2}$ . An increase in the fluence to  $5 \cdot 10^{17} \text{ cm}^{-2}$  (irradiation time of 5 min with a step of 1 min) results in melting of a NW bundle up to its middle, which is clearly observed in the scanning electron microscopy images (Figure 3 b). A further increase in the fluence (Figure 3 c) (irradiation time of 10 min with a step of 1 min) causes subsequent melting and deformation of NWs. Continuous irradiation with heating (Figure 3 d) (5 min) leads to the melting of the all surface of a NW bundle. The wires are less melted inside the bundle.



**Figure 3.** Scanning electron microscopy image of Ni NWs 60 nm in diameter after  $\text{Ar}^+$  ion irradiation with different fluences, heating to not higher than  $150^\circ\text{C}$  (accumulated fluences were achieved in several stages to avoid overheating): (a)  $F=10^{17}\text{cm}^{-2}$ ; (b)  $F=5\cdot 10^{17}\text{cm}^{-2}$ ; (c)  $F=10^{18}\text{cm}^{-2}$ ; and (d)  $F=5\cdot 10^{17}\text{cm}^{-2}$ , heating to a stationary temperature of  $550^\circ\text{C}$ .

Figure 4 shows  $\text{Fe}_{0.56}\text{Ni}_{0.44}$  NWs 100 nm in diameter after  $\text{Ar}^+$  ion irradiation. In this case, wires have a greater diameter; therefore, this seems to be the reason for their less deformation after irradiation. It is noticeable that tops of the wires are "sharpened" from the direction of beam irradiation at the increased fluence.

Figure 5 shows NWs irradiated with  $\text{Ar}^+$  and  $\text{Xe}^+$  ions for comparison purposes. In both cases, irradiation conditions were the same:  $E = 20\text{ keV}$ ,  $j = 300\text{ }\mu\text{A}/\text{cm}^2$ , a rotation rate of 8 rpm, an angle of  $45^\circ$ , heating to  $550^\circ\text{C}$ . Irradiation was performed in a continuous mode for 5 min. It can be seen from the figures that wires are noticeably deformed after  $\text{Xe}^+$  irradiation and are different from those irradiated with  $\text{Ar}^+$ .

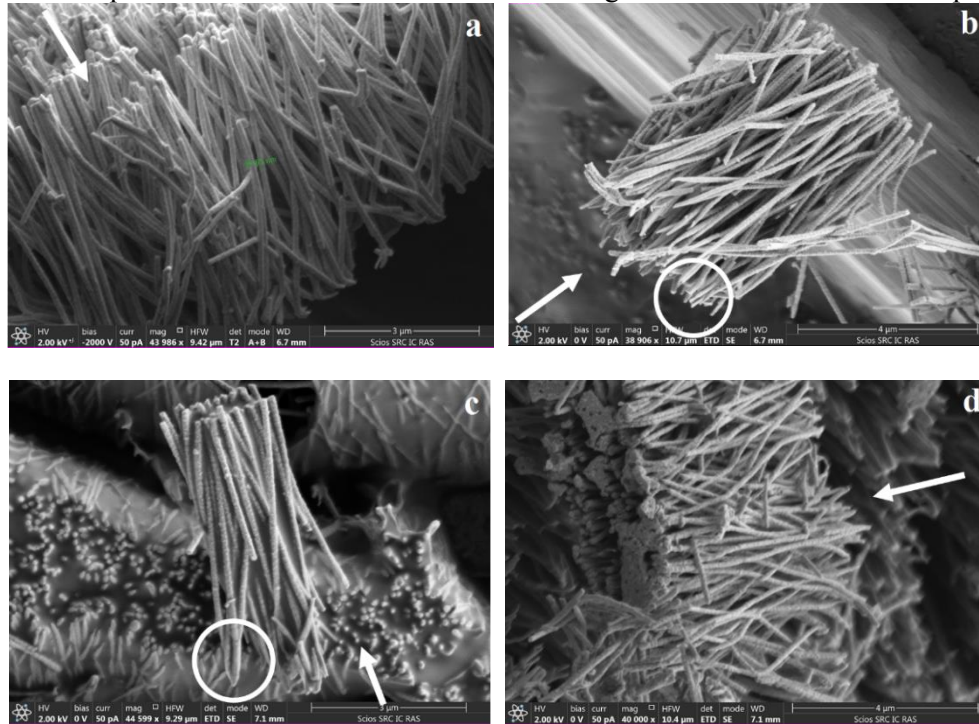
Taking into account the temperatures (150 and  $550^\circ\text{C}$ ), which are insufficient for melting pure nickel and iron-nickel alloy, the observed melting of nanowires can be explained by the formation of *thermal spikes* under irradiation with heavy ions [12, 13]. They are almost spherical (in the case of the implantation of heavy ions into heavy matrices) regions of dense cascades of atomic displacements with a typical diameter of 5-10 nm (about 9 nm for  $\text{Ar}^+$  and 6 nm for  $\text{Xe}^+$  [15] implanted in Ni with the used energy). The mentioned regions thermalized for  $10^{-12}\text{ s}$  (cooling time of  $\sim 10^{-11}$ ), reaching temperatures of 3000-5000 K and above. The average depth at which these regions are formed is about 5-10 nm at an ion energy of 20 keV.

Since the energy release per atom of the cascade is significantly higher in the case of  $\text{Xe}^+$  than that of  $\text{Ar}^+$  [15], Figure 5 shows more significant bending of nanowires with the formation of knots (buds) and even branches under  $\text{Xe}^+$  ion irradiation due to the possible splashes of the thermal peak regions out of the nanowires. Covering of adjacent nanowires with molten metal is possible.

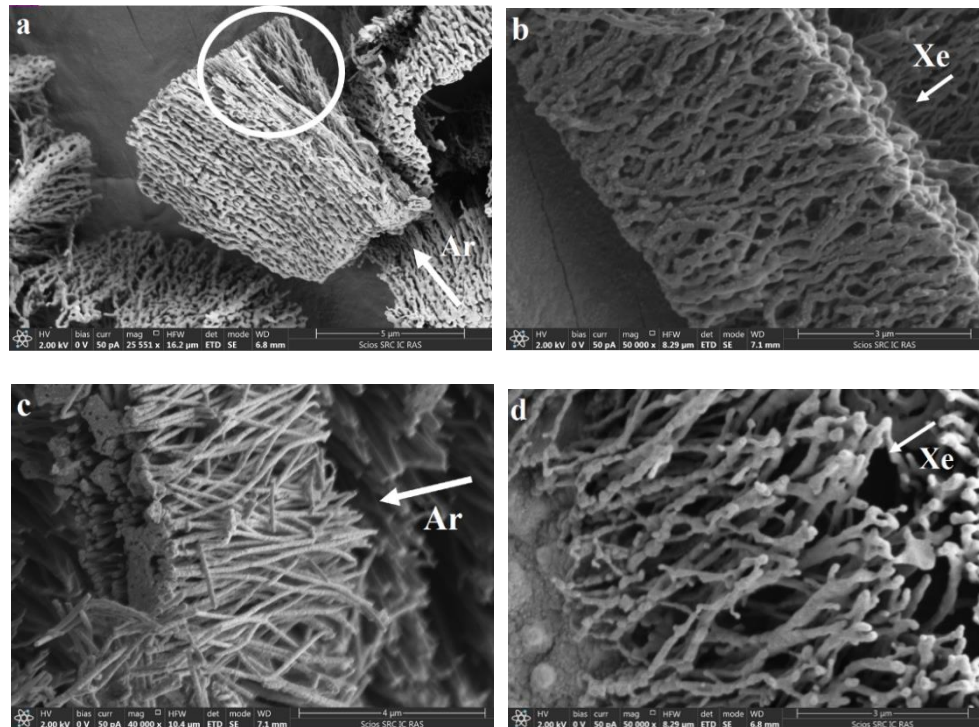
In view that the number of atoms per unit of the surface area of metals is  $\sim 10^{15}\text{ cm}^{-2}$ , we can conclude that the NW surface (which is not in the field of geometric shadow) has melted repeatedly at



fluences of  $10^{16}$ - $10^{18}$  cm $^{-2}$  due to the formation of thermal spikes [13, 14]. We put forward this mechanism as an explanation for the observed effect of melting of the NWs at low total temperatures.



**Figure 4.** Scanning electron microscopy image of Fe $_{0.56}$ Ni $_{0.44}$  alloy NWs 100 nm in diameter after Ar $^{+}$  ion irradiation with different fluences, with heating to 150°C: (a)  $F=10^{17}$  cm $^{-2}$ ; (b)  $F=5 \cdot 10^{17}$  cm $^{-2}$ ; (c)  $F=10^{18}$  cm $^{-2}$ ; and (d)  $F=5 \cdot 10^{17}$  cm $^{-2}$ , with heating to 550°C.



**Figure 5.** Scanning electron microscopy image of Ni NWs 60 nm in diameter and Fe $_{0.56}$ Ni $_{0.44}$  alloy NWs 100 nm in diameter after Ar $^{+}$  and Xe $^{+}$  ion irradiation with  $F = 5 \cdot 10^{17}$  cm $^{-2}$  (heating to 550°C).

It should be noted that damaged near-surface volume is comparable with the volume of nanowires (taking into account their rotation). There is an opinion that some decrease in the melting temperature may be caused by a sharp increase in the number of nonequilibrium defects in the NW volume. Although, it is evident that this mechanism cannot be the only explanation for the observed melting effect, but it can ease the melting process.

Note that damageable subsurface volume is comparable to a volume of NWs (in view of their rotation). Because of this, a marked decrease in the melting temperature may occur due to a sharp increase of the number of non-equilibrium defects in the volume of NWs. Although only this mechanism can hardly explain the observed melting effect, but it is also likely to contribute.

#### 4. Conclusions

As a result, the study showed that under both  $\text{Ar}^+$  and  $\text{Xe}^+$  ion irradiation conditions ( $E = 20 \text{ keV}$ ,  $j = 300 \mu\text{A}/\text{cm}^2$ , fluences of  $10^{16}$ - $10^{18} \text{ cm}^{-2}$ ), NWs are deformed and melted even upon slight general (not local) beam heating (to  $150^\circ\text{C}$ ). The effect of  $\text{Xe}^+$  ion irradiation is more pronounced.

As an explanation for the observed effect of melting of NW arrays at decreased temperatures we propose to consider the formation of thermal spikes under ion irradiation.

The conclusion about the low radiation stability of the NWs under used  $\text{Ar}^+$  and  $\text{Xe}^+$  ion irradiation conditions can be drawn. It is further interesting to study the effect of the chemical composition, the geometric characteristics of nanowires, the ion energy, and the kind of implanted ions on the radiation stability in detail. X-ray diffraction analysis and Mössbauer spectroscopy are required to obtain the information about possible amorphization of the NW surface by rapid quenching of thermal spikes and about other structural features of nanowires.

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